

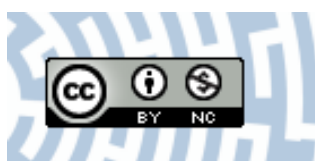


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# The newest clinical version of glass-polyalkenoate restorative biomaterial infused with 3Y-TZP nanocrystals

## Abstract

The aim of our study was to preliminarily investigate, in dental practice, the newest commercial formula of bioactive glass-ionomer cement modified with 3% mass of Yttrium Trioxide Partially Stabilized Tetragonal Polycrystalline Zirconia (3YTZP), which should improve restorative survival rate in caries patients' oral mouth, enhance translucence and match the color of the tooth. Initial laboratory observation has been performed with the use of microscopic structural analysis. By assumption novel dental restorative materials are expected to be indeed bioactive in the meaning of immanent enamel- and dentine-integration/adhesion without demineralization, saliva buffering, hard tissues remineralization and caries microbiome management ability, over a long period of time.

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## Introduction

This story begins more than 3.5 million (3.5x10<sup>9</sup>) years ago with the first Streptococci that were distinguishing from prokaryotes, and had come out of the oceans 570 million years in creatures as old as Paleozoic fishes, and left a mark on *Labidosaurus hamatus* - Mesozoic herbivores dinosaurs, a Pangaea animal circa 275 million years ago. *Homo rhodesiensis/heilderbergensis* also *Homo neanderthalensis* have already suffered from it in the period 650,000-100,000 BP. The thing is about nothing but caries disease.<sup>1-4</sup>

When caries disease leads to irreversible changes and defects in skeleton of the tooth, appropriate anatomical reconstruction is required, with the use of "smart materials" <sup>5</sup> preventing relapse, as they are to have a number of properties which may be altered in a controlled fashion in response to stimuli. These include ion exchange between external environment, inherent adhesion to hard tissues, buffering abilities, as well as a thermal expansion coefficient which is similar to teeth. Looking for such a dental biomaterial, glass ionomer cement (GIC) may seem to appear like a mainstream of evaluating restoratives as it adheres chemically to the tooth structure, controls pH and releases fluoride and other ions, hence it not only contributes to the reduction in the amount of residual bacteria underneath the restoration, but fundamentally favors remineralization of the affected dentin.<sup>6-8</sup>

Several thousand years ago humans could use primitive natural resources to fill holes in teeth with bitumen in what is nowadays Italy, or beeswax 6500 BP in what is today Slovenia.<sup>9,10</sup> In ancient Egypt 4600 BP, Hesy-Ra - 'Great one of the dentists', was able to prepare a mixture of terebinthine resin, powdered malachite and ochre from Nubian ground applied to the tooth.<sup>11</sup> The synthetic era starts with Marggraf's invention of nonorganic phosphoric acid 305 years ago, and an organic one - an acrylic acid, the discovery of which we owe to Redtenbacher 175 years ago. Linderer's son<sup>12</sup> 167 years ago mentioned the use of semisynthetic cement: ground enamel of carnivorous animal made into a paste with phosphoric acid. The first true synthetic cement was the zinc oxychloride invented by Sorel 163 years ago.<sup>13</sup> Smith 55 years ago researched on poly(acrylic acid) salt of sintered zinc

oxide, which after 5 years has been fortunately introduced into dental practice as zinc polycarboxylate - first biomaterial with the intention of adhesive bonding to tooth hydroxyapatite calcium.<sup>14</sup>

The contemporary GICs were developed over 50 years ago, starting by Wilson and co-workers at the Laboratory of The Government Chemist (LGC) in London and introduced into the clinic use by Mc Lean, as materials consisting of an acid-decomposable glass and a water-soluble acid that sets into salt by neutralization reaction. The term glass-ionomers covers two subgroups: glass-polyalkenoates and glass-phosphonates.<sup>15-18</sup> GICs have been first used to repair dental defects, however later have been introduced in otological and neuro-otological surgery and injectable bone cements as Al-free formulations with the inclusion of ZnO, GeO<sub>2</sub>, ZrO<sub>2</sub>, and Na<sub>2</sub>O into the glass network, with potential metal cations release within a window of concentrations that promote osteoblast.<sup>19-21</sup>

Taking into the consideration the development of commercial GICs chemical composition modifications, conventional (CGIC), metal-reinforced (-RGIC), fast setting (FSGIC), cermet-ionomers, semi- and anhydrous (WAGIC), high viscosity (HVGIC), visible-light-activated (VLGIC), resin-modified (RMGIC - dual and tree-cured DCRMGIC and TCRMGIC), glass carbomers (GCC), ceramics-, or zirconia-reinforced GIC might be chronologically distinguished.<sup>22-29</sup> The latter one is intended to be of higher strength compared with that of amalgam silver. It turned out that the glass-ionomer with the addition of 7% by weight ceramic granules showed promising VMHT values of hardness 58.98 MPa, DTS of tensile 11.21MPa and compressive strength results of CS after one month 423 MPa.<sup>30-32</sup>

## Methods

The newest formula with 3% mass of Yttrium Trioxide Partially Stabilized Tetragonal Polycrystalline Zirconia (3YTZP) has been approved for use in dental clinic as Zirconomer Improved (Shofu Inc, Kyoto, Japan) - zirconia-reinforced glass ionomer cement of CS 326 MPa,<sup>33</sup> which should improve survival rate in oral mouth, enhance translucence and match the color of the tooth; the fluid of Zirconomer Improved is a water solution of poly(acrylic acid) (PAA) and tartaric

acid (TA). The Zirconomer family of materials is supplied in the form of powder and liquid for manual earning, although encapsulated versions have appeared on the market. The surface of the material should, after solidification, be covered with a protective layer of cocoa butter. Zirconomer Improved universal shade was used for the secondary caries treatment. Biomaterial was prepared according to the manufacturer's instruction for clinical restoration and caries treatment of tooth 25. Preliminary, non-clinical structural microscopic analysis was performed. Metallographic microscope Olympus GX51 was used with magnifications:  $\times 10$ ,  $\times 20$  and  $\times 50$ , resolution of the effective camera 10.6 megapixels, reverse microscope system, observations in a bright field reflected light and optics adjusted to the infinity of UIS-2.

## Results and discussion

Zirconia-reinforced glass-ionomer has been successfully utilized as bioactive core restoration (Figure 1) in short-time observation in adult patient of active caries disease. Microscopic observation confirmed fine submicronic grain structure of glass particles with nano sized ceramic crystals (Figure 2). Glassy-depleted zirconia ceramics based on a polycrystalline milky zirconia powder, called 'ceramic steel', is a clue of modern restorative dentistry. Its mechanical properties and physical parameters: bending strength (840-1400MPa), modulus of elasticity (200GPa), stress intensity factor 9-10 MPa/m, Vickers hardness (13GPa), compressive strength (2,100MPa), Tensile strength (650 MPa), fatigue strength (900 MPa), fracture toughness (9 MPa/m  $1/2$ ) inspire admiration as they are close to or even exceed the metal alloys. To stabilize the tetragonal metastable polycrystalline structure during thermo-dependent transformation the homogenously distributed cerium, yttrium, aluminum, magnesium or calcium oxides are added to prevent material aging by spontaneous and unwanted transformation of the TM into a monoclinic phase (up to 25%) by reacting water with oxygen-zirconium chains at the temperature of the human body, moist environment of the mouth, spongy bone and under the influence of mechanical stress. Aging zirconia may result in a loss of up to 50% of the original strength values and an increase in the volume of 3-5%, which may paradoxically compensate for the propagation of potential cracks generated in the material by auto repair. Fully stabilized cubic zirconia (FSZ) is produced with the participation of oxides: 7.9% by weight of CaO or 5.86 by weight of MgO or 13.75 by weight of  $Y_2O_3$ ; each smaller contribution leads to a partially stabilized zirconia (PSZ) called tetragonal polycrystalline zirconia, most often with yttrium trioxide (YTZP). Tetragonal polycrystalline zirconium doped with 3-5% by weight is commonly used.<sup>34</sup>



**Figure 1** a) Tooth 25, patient FK, deep caries lesion; b) fresh after bioactive restore; c) after 12 weeks.

Glass-ionomers are bio-degradable/resorbable biomaterials. Due to this slow, but possibly reversible in the ecosystem, oral disintegration, they show active bioactivity, owing to which remineralization of dentin and enamel is possible, saliva buffering, stabilization of cariogenic flora and as a result the ability to control the fit of active caries to

stationary caries. If the addition of nanometric zirconia to the GIC composition strengthens their strength, it will be beneficial for them against carious use, in at least several dozen months perspective of permanent biochemical-physical dentin-and enamel integration, even if they are classified as materials for temporary fillings. It is worth perceiving the glass-ionomer qualities and functions resulting from them, qualifying them for the role of the first-choice biomaterials in the treatment of active acute carious disease. In the long-term treatment of a patient with caries, we should additionally re-educate diet and hygiene habits, balance both the immune system and mineral balance.



**Figure 2** Microstructure of fresh set biomaterial in different magnifications:  $\times 10$ ,  $\times 20$ ,  $\times 50$ .

## Conclusion

We still have to solve an important issue, which is the selection of the restorative material. Should we choose silver amalgam, which is a filling from a piece of mercury alloy, but, in turn, does not cure caries? Are we to choose nice light- or chemo-curing composites, most often based on bacteriophilic monomers, requiring additional etching species i.e. deepening the enamel and dentine caries effect, which also do not cure caries? Is it just to choose glass-ionomers, which although are included in tooth-colored restorative materials, but are not to serve as high aesthetic materials and compete in this respect with ceramic-monomer composites in carries-free patients? As a matter of fact such glass-ionomers are immanently resorbable polyelectrolytes of active caries management ability in assumption; therefore their restorative long-term attributes would not have to play a primary role.

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## Conflict of interest

Study has not been ordered, financed and there is no conflict of interest.

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